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(57) Abstract

By blending a first polyolefin, or an interpolymer thereof, which is of low melt index and is multi–modal in molecular weight distribution, with a homogeneous polyolefin which is compatible in melt mergibility with the first polyolefin, and co–extruding or extruding through a flat slot die the blend, with or without a second polyolefin, or an interpolymer thereof, a laminate or a monolayer is obtained. The laminate comprises a structural layer comprised of the first polyolefin, or the interpolymer thereof, and a sealant layer comprised of the second polyolefin or the interpolymer thereof, having a seal–initiation temperature lower than the seal initiation temperature, or at least the thermoforming temperature plateau, of the structural layer and compatible in melt mergibility with the structural layer. The monolayer or the laminate is particularly suitable for thermoforming into containers.

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POLYOLEFIN FILMS AND LAMINATES

This invention relates to one or more layers, to a method of producing the same and to a method of using the same. The invention is concerned particularly, but not exclusively, with one or more layers in the form of a web suitable for thermoforming, especially a packaging laminate to be thermoformed.

There are generally used in thermoforming systems for sheet-form packaging material, substances such as polypropylene (PP), polystyrene (PS), polyester and combinations thereof.

Known sheet thermoforming systems include tray-forming systems in which a single sheet is formed using heat and pressure and/or vacuum; these tray-forming systems include systems in which the tray is formed on a form-fill-seal (FFS) machine. Other systems are those in which two sheets (which may be two separate webs or a single web folded upon itself) are thermoformed in a mould and sealed together around outlines of the containers, or sealed around the outlines and then thermoformed in the mould.

It is also known to employ a homogeneous polyolefin to modify properties of sealant layers. For example, WO-A-95/21743 discloses a multilayer film, of a thickness of between 40 and 130 microns, and a pouch containing a flowable material. The multilayer film is made from two layers of a sealant film with an interposed layer of a polyethylene. The sealant film is made from a material comprising 10 to 100 parts by weight of a copolymer of ethylene and at least one C_4-C_{10} alpha-olefin manufactured in a polymerization process using a single-site polymerization catalyst and from 0 to 90 parts by weight of at least one polymer selected from the group consisting of a linear copolymer of ethylene and at least one C_4-C_{10} alpha-olefin having a density of from 0.900 to 0.930 g/cm^3 and a melt index of from 0.3 to 2.0, a high-pressure polyethylene having a density of from 0.916 to 0.930 g/cm^3 and a melt index of from about 1 to 10, and blends thereof. The polyethylene of the interposed layer is a high density polyethylene with a density of at least 0.930 g/cm^3

and a melt index of less than 5. The pouch is made from the multilayer film and has transversely sealed ends. The pouches are particularly useful in the packaging of flowable materials e.g. milk, especially using a vertical form, fill and seal apparatus.

High density polyethylene (HDPE) as generally used in extrusion of film, which is not subsequently to be thermoformed, is typically of Type III or IV, Categories 4 and 5, as defined in ASTM (American Society for Testing and Materials) D1248-84. It is known to increase the melt strength of the HDPE by increasing the average molecular weight.

HDPE as generally used in sheet extrusion for subsequent thermoforming is typically of Type III or IV, Category 3 (ASTM D1248-84). Such HDPE has poor thermoforming characteristics and, on blow-thermoforming machines in which two HDPE strips are brought together and blow-thermoformed, has poor sealing characteristics. Its poor thermoforming characteristics arise from its low melt strength - the portion of the visco-elastic plateau which is suitable for thermoforming is narrower than is desirable. Its poor sealing characteristics arise from its having a seal-initiation temperature which is above its thermoforming temperature plateau and its having a low melt strength at its sealing temperature, such that the sealing pressure of sealing jaws, for example, causes them to penetrate through the HDPE. The softening of the HDPE at its sealing temperature results in great difficulty in transporting such strip through the machine without elongation or other deformation of the strip.

Attempts have been made to improve the thermoforming characteristics of sheet HDPE by increasing the melt strength through increasing the average molecular weight. However this has been found to lead to an increase in thermal retraction [as defined in NF (Norme Française Enregistrée) T54-105, April 1973, condition 130°C] actually worsening the thermoforming characteristics.

However, HDPE is desirable as a packaging substance for a number of reasons, for example because it is readily acceptable in recycling schemes and waste disposal systems,

is readily available and inexpensive, and is relatively light in specific weight.

According to a first aspect of the present invention, there is provided a method comprising providing a laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than that of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, and thermoforming said laminate.

According to a second aspect of the present invention, there is provided a method comprising providing a laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than the thermoforming temperature plateau of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, and thermoforming said laminate.

In relation to these two aspects of the invention, we have surprisingly found that a laminate similar to laminates known as films can be manufactured of sheet thickness suitable for thermoforming. The advantage of using the first polyolefin or the interpolymer thereof, as set out above, is that it thermoforms well, so that it is possible to form containers, e.g. trays, with very high barrier to transmission of water vapour as well as good hot fill capabilities. The inclusion of the sealant layer has the advantage that the processing on FFS machines is significantly improved.

According to a third aspect of the present invention, there is provided a method comprising co-extruding through a flat slot die a first polyolefin, or an interpolymer thereof, which is of low melt index and is multi-modal in molecular weight distribution, and a second polyolefin, or an

interpolymer thereof, to provide a laminate comprising a structural layer comprised of said first polyolefin, or said interpolymer thereof, and a sealant layer comprised of said second polyolefin or said interpolymer thereof, having a seal-initiation temperature lower than that of said structural layer and compatible in melt mergibility with said structural layer.

According to a fourth aspect of the present invention, there is provided a method comprising co-extruding through a flat slot die a first polyolefin, or an interpolymer thereof, which is of low melt index and is multi-modal in molecular weight distribution, and a second polyolefin, or an interpolymer thereof, to provide a laminate comprising a structural layer comprised of said first polyolefin, or said interpolymer thereof, and a sealant layer comprised of said second polyolefin or said interpolymer thereof, having a seal-initiation temperature lower than the thermoforming temperature plateau of said structural layer and compatible in melt mergibility with said structural layer.

Owing to these two aspects of the invention, it is possible to produce a laminate by co-extrusion which does not require an adhesive layer between the structural layer and the sealant layer, so simplifying the production process. Moreover, if the co-extrusion from the die is downwards into a calender roll stack it is possible to obtain very tight tolerance of sheet thickness. Sheet of the laminate, most surprisingly, has good thermoformability characteristics as well as good sealability characteristics. In particular, it is surprising that, although a low melt index would be expected to result in a high thermal retraction, which would make the structural layer difficult to thermoform, the present structural layer has a low thermal retraction.

According to a fifth aspect of the present invention, there is provided a laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than that of said structural

layer and comprised of a second polyolefin, or an interpolymer thereof, the substance of said structural layer being multi-modal in short chain branching distribution.

According to a sixth aspect of the present invention, there is provided a laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than the thermoforming temperature plateau of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, the substance of said structural layer being multi-modal in short chain branching distribution.

Owing to these two aspects of the invention, an improved laminate can be obtained.

According to a seventh aspect of the present invention, there is provided a laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than that of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, said structural layer incorporating a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

According to an eighth aspect of the present invention, there is provided a laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than the thermoforming temperature plateau of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, said structural layer incorporating a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

According to a ninth aspect of the present invention, there is provided a layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and which incorporates a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

According to a tenth aspect of the present invention, there is provided a method comprising a layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and which incorporates a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin, and thermoforming said layer.

Very surprisingly, because homogeneous polyolefins generally are noted for their low melt strength, the incorporation of the homogeneous polyolefin in the (structural) layer improves the thermoformability of the (structural) layer.

The layer may be in the form of a monolayer or may be one layer of a laminate. The laminate may include a sealant layer, one or more tie layers, or a barrier layer (such as EVOH or PA); it could also contain additives (such as peelability additives, pigments, UV filters, oxygen scavengers, and anti-microbial agents).

The monolayer or the laminate is preferably of a thickness of at least 100 microns, more preferably of a thickness of at least 200 microns, so that it constitutes sheet rather than film.

The melt index of the first polyolefin is preferably lower than 0.8g/10mins., especially lower than 0.45g/10mins., at ASTM D1238-95, Conditions 190/2.16 for HDPE, and preferably lower than 8g/10mins, especially lower than 5g/10mins, at ASTM D1238-95, Conditions 230/2.16 for PP.

Most preferably, the substance of the monolayer or the structural layer is multi-modal (e.g. bi-modal) in short chain branching distribution. The first polyolefin may comprise PP, but preferably comprises HDPE of Type III or IV, Category 4 or 5, preferably Category 5, of ASTM D1248-84.

That HDPE has the advantage of having very good impact properties down to temperatures of minus 80°C.

The first polyolefin may be modified by incorporating a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with the first polyolefin. The homogeneous polyolefin may be PP or PE where the first polyolefin is PP or HDPE, and is preferably present in an amount of between 2 and 50% by weight, particularly between 10 and 30% by weight. Very surprisingly, because homogeneous polyolefins generally are noted for their low melt strength, this modification improves the thermoformability of the laminate.

The polyolefin of the sealant layer would advantageously comprise PP or PE in the event that the polyolefin of the structural layer comprises PP, or would advantageously comprise PE in the event that the polyolefin of the structural layer comprises HDPE. In the former event, the polyolefin of the sealant layer preferably comprises an interpolymer of PP; in the latter event, it preferably comprises LDPE (low density polyethylene) or LLDPE (linear low density polyethylene) or homogeneous PE or blends thereof, and optionally may include one or more additives, for example a peelability additive, e.g. polybutylene or ionomer.

In the case of use of the laminate in a blow-thermoforming process, the sealant layer should have a seal-initiation temperature at least 1°C, preferably at least 5°C, below the thermoforming temperature plateau, preferably the seal-initiation temperature, of the structural layer.

Homogeneous polyolefins are polyolefins which, in respect of their compositions and/or manufacture, are best exemplified by Elston in US-A-3645992; Canich in US-A-5026798 and US-A-5055438; Stevens et al. in US-A-5064802; and by the products known as "TAFMER"® available from Mitsui Petrochemical Co. Ltd.,"AFFINITY"® and "ENGAGE"® available from The Dow Chemical Company and the metallocene polyethylenes manufactured using the "EXPOL"® process by Exxon Corporation.

The present laminate is particularly, but not

exclusively, applicable to FFS machines.

In order that the invention may be clearly understood and readily carried into effect, an example thereof will now be described.

A packaging laminar web is formed by co-extrusion of, in order from the outside to the inside, an HDPE blend [of HDPE (grade reference HDPE 35057E as supplied by The Dow Chemical Company) 86%, "AFFINITY"® PL1880 homogeneous PE 10% and Cabot PE7024 white pigment masterbatch 4% by weight], a PE graft interpolymer tie layer, an EVOH (ethylene vinyl alcohol) barrier layer, a PE graft interpolymer tie layer, and an LDPE blend [of LDPE (grade reference "LACQUTENE" LD0304 as supplied by Atochem) 84% and Shell PB8240 polybutylene 16% for peelability], to provide a laminate of an HDPE blend structural layer 270 microns thick, an outer tie layer 15 microns thick, an EVOH barrier layer 20 microns thick, an inner tie layer 15 microns thick and an LDPE blend sealant layer 30 microns thick.

If the EVOH barrier is not required, the outer and inner tie layers and the barrier layer may be omitted, because the HDPE blend readily heat-merges with the LDPE blend (it being generally known that HDPE readily heat-merges with LDPE).

Two identical such webs were brought together, sealant layer-to-sealant layer, on a "UNIFILL" TR 86 thermoforming machine and the container outlines sealed at a temperature of 130°C, at which a successful seal was achieved between the sealant layers, and the webs were successfully thermoformed into yoghurt containers of 30cc.

CLAIMS

1. A method comprising providing a laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than that of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, and thermoforming said laminate.

2. A method comprising providing a laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than the thermoforming temperature plateau of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, and thermoforming said laminate.

3. A method according to claim 1 or 2, wherein said providing comprises co-extruding the substance to form said structural layer and the substance to form said sealant layer.

4. A method according to claim 3, wherein the co-extrusion from said die is downwards into a calender roll stack.

5. A method according to any preceding claim, wherein said providing comprises blending said first polyolefin, or said interpolymer thereof, with a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

6. A method comprising co-extruding through a flat slot die a first polyolefin, or an interpolymer thereof, which is of low melt index and is multi-modal in molecular weight distribution, and a second polyolefin, or an interpolymer thereof, to provide a laminate comprising a structural layer comprised of said first polyolefin, or said interpolymer thereof, and a sealant layer comprised of said second polyolefin or said interpolymer thereof, having a seal-initiation temperature lower than that of said structural layer and compatible in melt mergibility with said structural

layer.

7. A method comprising co-extruding through a flat slot die a first polyolefin, or an interpolymer thereof, which is of low melt index and is multi-modal in molecular weight distribution, and a second polyolefin, or an interpolymer thereof, to provide a laminate comprising a structural layer comprised of said first polyolefin, or said interpolymer thereof, and a sealant layer comprised of said second polyolefin or said interpolymer thereof, having a seal-initiation temperature lower than the thermoforming temperature plateau of said structural layer and compatible in melt mergibility with said structural layer.

8. A method according to claim 6 or 7, wherein the co-extrusion from said die is downwards into a calender roll stack.

9. A method according to any one of claims 6 to 8 and further comprising, before said co-extruding, blending said first polyolefin, or said interpolymer thereof, with a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

10. A laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than that of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, said structural layer incorporating a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

11. A laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than the thermoforming temperature plateau of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, said structural layer incorporating a minor amount of a

homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

12. A laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than that of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, the substance of said structural layer being multi-modal in short chain branching distribution.

13. A laminate comprising a structural layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and a sealant layer compatible in melt mergibility with said structural layer, having a seal-initiation temperature lower than the thermoforming temperature plateau of said structural layer and comprised of a second polyolefin, or an interpolymer thereof, the substance of said structural layer being multi-modal in short chain branching distribution.

14. A laminate according to claim 12 or 13, wherein said structural layer incorporates a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

15. A laminate according to claim 10, 11, or 14, wherein said homogeneous polyolefin is present in said structural layer in an amount of between 2 and 50% by weight.

16. A laminate according to claim 15, wherein said amount is between 10 and 30% by weight.

17. A laminate according to any one of claims 10 to 16, and of a thickness of at least 100 microns.

18. A laminate according to claim 17, and of a thickness of at least 200 microns.

19. A laminate according to any one of claims 10 to 18, wherein said first polyolefin comprises high density polyethylene.

20. A laminate according to claim 19, wherein said high density polyethylene is of Type III or IV, Category 4 or 5,

of ASTM D1248-84.

21. A laminate according to claim 19 or 20, wherein said high density polyethylene has a melt index lower than 0.8.

22. A laminate according to claim 21, wherein said melt index is lower than 0.45.

23. A laminate according to any one of claims 19 to 22, wherein said second polyolefin comprises polyethylene.

24. A laminate according to claim 23, wherein said second polyolefin is selected from the group consisting of low density polyethylene, linear low density polyethylene, homogeneous polyethylene and blends thereof.

25. A laminate according to any one of claims 10 to 18, wherein said first polyolefin comprises polypropylene.

26. A laminate according to claim 25, wherein said polypropylene has a melt index lower than 8.

27. A laminate according to claim 26, wherein said melt index is lower than 4.

28. A laminate according to any one of claims 25 to 27, wherein said second polyolefin comprises polypropylene.

29. A laminate according to claim 28, wherein said second polyolefin comprises an interpolymer of polypropylene.

30. A layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and which incorporates a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin.

31. A layer according to claim 30, wherein the substance of said layer is multi-modal in short chain branching distribution.

32. A layer according to claim 30 or 31, wherein said homogeneous polyolefin is present in said layer in an amount of between 2 and 50% by weight.

33. A layer according to claim 32, wherein said amount is between 10 and 30% by weight.

34. A layer according to any one of claims 30 to 33, and of a thickness of at least 100 microns.

35. A layer according to claim 34, and of a thickness of at least 200 microns.

36. A layer according to any one of claims 30 to 35, wherein

said first polyolefin comprises one of polypropylene and high density polyethylene.

37. A layer according to claim 36, wherein said high density polyethylene is of Type III or IV, Category 4 or 5, of ASTM D1248-84.

38. A layer according to claim 36 or 37, wherein said high density polyethylene has a melt index lower than 0.8.

39. A layer according to claim 38, wherein said melt index is lower than 0.45.

40. A laminate according to claim 36, wherein said polypropylene has a melt index lower than 8.

41. A laminate according to claim 40, wherein said melt index is lower than 5.

42. A method comprising providing a layer comprised of a first polyolefin, or an interpolymer thereof, which is of a low melt index and is multi-modal in molecular weight distribution, and which incorporates a minor amount of a homogeneous polyolefin which is compatible in melt mergibility with said first polyolefin, and thermoforming said layer.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B27/32 C08L23/06 C08L23/10 C08J5/18

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L C08J B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 21743 A (DU PONT CANADA ;BRECK ALAN KEITH (CA); VERDONE ALANA (CA)) 17 August 1995 cited in the application see page 11, line 6 - line 15 see page 11, line 34 - page 12, line 12 see page 17, line 10 - page 19, line 15; claims	1
X	FR 2 154 634 A (DU PONT CANADA) 11 May 1973 see claims	1
X	US 5 382 631 A (STEHLING FERDINAND C ET AL) 17 January 1995 see column 23, line 38 - column 24, line 48; claims 1,8	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
8 January 1998	28/01/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	De Jonge, S

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte >nal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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